

# CHEMICAL ANALYSIS BY X-RAYS<sup>1</sup>

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In the earlier days of the century pioneer work such as that of Moseley (1913), von Hevesy (1932) and von Hevesy and Alexander (1933) opened up tantalizing possibilities for rapid, efficient, and accurate chemical analysis. It is an interesting fact that during the ensuing thirty years of intensive instrumental development these possibilities remained largely beyond the grasp of workers in the physical sciences. Only recently have methods of x-ray production, utilization, and measurement evolved to the degree that some of the promises can be realized in practice. It is the purpose of this paper to review the progress of x-ray analysis, to emphasize its unique advantage in certain cases, and to indicate directions in which developments are proceeding at the present time. There will be no attempt at an exhaustive survey of the field.

Two broad classifications of chemical analysis by x-rays may be distinguished, which we might call ultimate analysis and compound analysis. The former tells us what chemical elements are present in the sample, irrespective of their chemical combination, and, if we wish, the percentage composition. Compound analysis yields information not only on the elementary composition but also gives the particular chemical compound. By this means, for example, we could determine that a certain white crystalline powder is composed of a mixture of NaBr and KCl and not NaCl and KBr. Compound analysis likewise can be made to give quantitative results by use of the proper techniques.

Both ultimate and compound analyses depend for their principles of operation on the diffraction of x-rays by crystals. It will be recalled that a crystal may be thought of as consisting of a multitude of layers or planes of atoms, each plane separated from its neighbor by a grating space,  $d$ , characteristic of the crystal. These many layers may cooperate in such a way that the atomic planes appear to an incident x-ray beam very much the same as does an ordinary mirror to a beam of light. If, then, a monochromatic beam of x-rays of wavelength  $\lambda$  is incident on these atomic planes at an angle  $\theta$ , specular reflection will occur *provided* that in addition the following condition is satisfied, namely,

$$n\lambda = 2d \sin \theta. \quad (1)$$

In this equation, the so-called Bragg equation,  $n$  is an integer, called the *order* of reflection and in practice rarely exceeds 4 or 5. If the incident beam is heterogeneous in wavelength *only those wavelengths satisfying Eqn. 1 will be reflected* for any given angle of incidence. The remainder of the beam will continue on into the crystal and eventually be absorbed. By varying the angle  $\theta$ , then, one can sweep through the spectrum and determine which x-ray wavelengths are present.

Using these principles of operation W. H. Bragg and his son, W. L. Bragg (1913), constructed the spectrometer shown schematically in figure 1 for the analysis of x-ray emission spectra from various elementary targets. This design principle is of particular interest to us, for it is still in use in the popular and effective North American Philips Geiger Counter Spectrometer, of which we will have more to say presently.

In the Braggs' original spectrometer the x-rays were generated in a gas type x-ray tube, the only kind known at the time. The ionization chamber has such

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an angular position with respect to the crystal planes that any radiation in the incident beam which is reflected from the crystal according to Eqn. 1 will enter the ionization chamber. By a gearing arrangement the ionization chamber is made to move at twice the angular velocity of the crystal table so that this relation is preserved at all Bragg angles.

In their book the Braggs (1925) consider both the case in which the crystal C in figure 1 is a large single crystal and that in which C is a powdered crystal and discuss the difference in the resulting curve of the reflected intensity versus the Bragg angle.

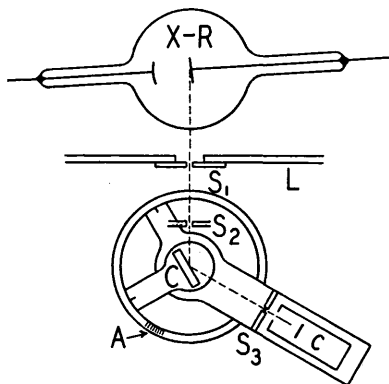


FIGURE 1. Bragg X-Ray Spectrometer.  $S_1$ ,  $S_2$ ,  $S_3$ , defining slits; L, shielding lead box surrounding the tube; C, analyzing crystal; IC, ionization chamber; A, divided circle.

#### ULTIMATE ANALYSIS

In their early experiments the Braggs (1913) showed that a typical emission spectrum from a single element has two components (fig. 2). The first, the *continuous* or "white" spectrum, has a diffuse distribution in wavelength, starts abruptly at the short wavelength limit, whose position is determined solely by the target potential applied to the x-ray tube, rises to a broad maximum and trails away at long wavelength. The *characteristic* spectrum, superposed on the continuous, is in sharp contrast, for it consists of narrow, intense "lines," whose wavelengths are characteristic of the target material alone. Each element has its own characteristic spectrum. The lines are separated into groups, usually called *series*, the shortest wavelength series being named the K series, followed by the L, M, N, . . . series.

Figure 2 gives the entire K series of iron. Its utter simplicity as compared with the ordinary arc spectrum in the visible region, containing thousands of lines, is a noteworthy feature. The precise measurement of the wavelength of any one of the x-ray lines provides certain identification of the presence of iron in the target material. The presence of other elements has none but the minutest effect on the wavelength or shape of these lines. This, for the most part, is a separate subject and will not concern us.

The problem of ultimate analysis by emission, stated simply, is: To produce characteristic x-radiation from the sample, to analyze this radiation into a spectrum by crystalline reflection (or other means) and to detect, measure and interpret the spectral distribution in terms of the elementary constitution of the sample and the relative percentages. In principle the solution to this problem has been well known for some years for the great majority of elements from Be(4) to U(92) and higher. As a matter of ordinary laboratory routine the complete solution is still nowhere in sight; but if we will be content with something less than perfection x-ray analysis can be of very considerable value to the routine analyst.

Several treatises (von Hevesy, 1932; von Hevesy and Alexander, 1933; Glocker, 1936; Clark, 1940) and many papers have been written on x-ray analysis. The attention of the reader is called particularly to the lists of advantages and disadvantages of x-ray analysis in Professor Clark's book. It will become clear as this article proceeds that modern techniques have relinquished none of the advantages and have eliminated not a few of the disadvantages. The difficulties inherent in the method have been subjected to close scrutiny and necessary precautions outlined. The application of the method to any particular problem in analysis must be studied by the prospective user if he is to have reasonable certainty of success. Once applied properly, however, the method is simple, foolproof and gives a unique answer. In routine cases anyone of ordinary intelligence can quickly learn to perform the necessary manipulations.

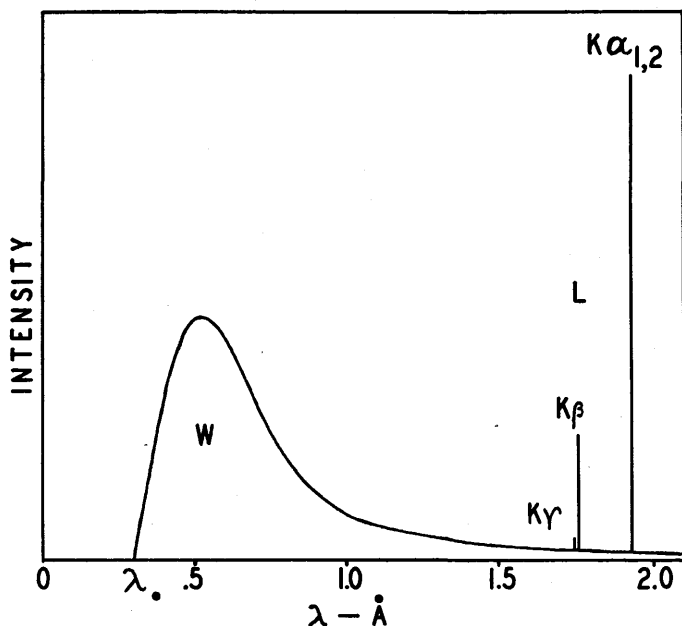


FIGURE 2. Intensity *vs.* wavelength from an iron target showing the continuous spectrum, W, with its short wavelength limit,  $\lambda_0$ ; and the K characteristic spectrum L. Relative intensities are only indicative. A target potential of 40 KV is assumed.

Chemical analysis by x-rays as described in the above treatises might be referred to as "classical analysis." Here, for the most part, the photographic plate or film is used for registration of the spectra. Clark (1940) lists four possibilities for x-ray excitation of the sample:

1. The sample is made the target of the x-ray tube and direct electron bombardment is used.
2. Secondary fluorescent emission is excited by placing the sample *inside* the x-ray tube in such a position that it is screened from the cathode rays but subjected to primary x-radiation from the target.
3. Secondary fluorescent emission is excited by placing the sample outside the x-ray tube immediately in front of the window.
4. Cathode rays emerging from the tube through a very thin window produce electron bombardment excitation of the sample outside of the tube.

Of these methods Nos. 1 and 2 will give the greatest intensity of x-rays but require a demountable tube with its attendant pumps and troubles. We must

discard consideration of these methods if we are going to speed up and simplify the process. No. 4 is strictly a laboratory technique and must be disregarded.

We are left with the single choice of the third alternative, with its attendant disadvantage of low radiation intensity. If, in addition, we must depend on photographic registration of the spectra the method becomes too slow and tedious and insensitive to be practical in routine analysis. This was the situation until the Geiger Counter (Korff, 1946) and the Scintillation Detector (Hofstetter and McIntyre, 1950) were developed into dependable measuring instruments during the last ten years.

Both the Geiger Counter and the Scintillation Detector have the unique advantage that they detect and register single x-ray quanta which enter the

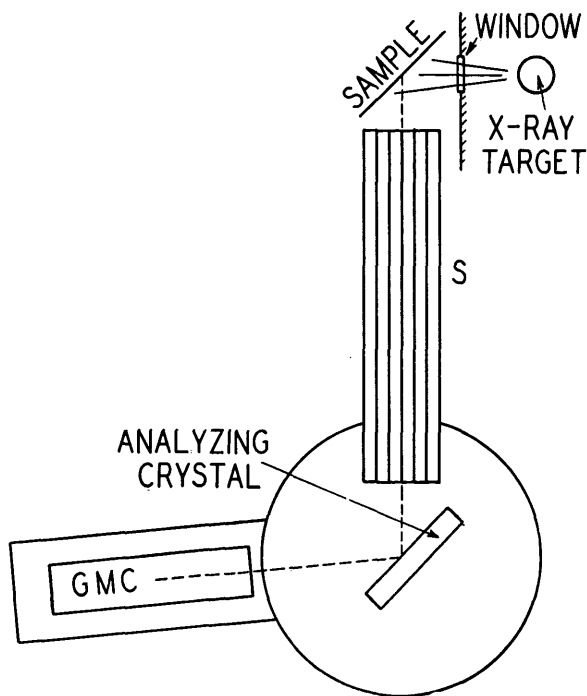


FIGURE 3. Schematic diagram of Friedman's (1948) arrangement for ultimate analysis by fluorescent x-rays. The multiple slit S is described in the text.

detector. In the case of the Geiger Counter the x-ray quantum enters the tube through a transparent window and, upon absorption in the gas contained in the tube, starts an electrical discharge between two electrodes provided for the purpose. Provision is made to extinguish the discharge after ten to a hundred microseconds and the resulting pulse of electrical charge actuates an electronic relay to record the arrival of the x-ray quantum. The x-ray intensity is recorded automatically as the number of quanta entering the Geiger Counter per second of time. Geiger counters suitable for x-ray detection with their attendant electrical circuits are available as standard equipment from manufacturers of x-ray equipment.

The Scintillation Detector is not yet in commercial use on a wide scale. The principle depends upon the well-known fact that when certain crystals absorb an x-ray quantum a flash of light is emitted. This fact is, of course, made use of in the ordinary x-ray fluoroscope used by the medical profession. The Scintillation

Detector uses a photomultiplier tube, such as the RCA 5819, to detect the flash of light and record it as an x-ray quantum absorbed in the crystal. Again, the number of such quanta registered per second is a measure of the x-ray intensity. The Scintillation Detector has several attractive advantages over the Geiger Counter. The quantum is registered in no more than one microsecond, and the system is then prepared to register another quantum. For this reason, then, a considerably higher intensity can be recorded with the Scintillation Detector than with the Geiger Counter. A second point is that no entrance window to the crystal is required. This would be especially desirable for recording very soft x-rays, as we will see presently.

Friedman and Birks (1948) have explored some of the possibilities of the method using the apparatus shown schematically in figure 3. The sample under investigation is placed outside the tube and as close to the window as possible.

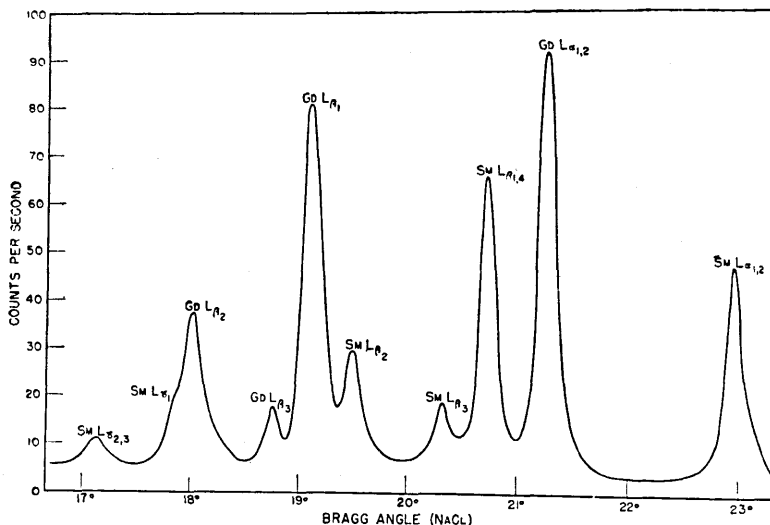


FIGURE 4. Fluorescence spectrum of the L series lines of a mixture of samarium (62) and gadolinium (64) salts (after Friedman, 1948).

The multiple slit S, through which the secondary radiation passes to the analyzing crystal, is made of a bundle of small diameter, thin walled nickel tubing. This produces a satisfactorily parallel beam of fluorescent x-rays. The Geiger Counter is arranged to receive the x-rays reflected at the Bragg angle from the analyzing crystal of rock salt or fluorite. The x-ray intensity is recorded on an automatic chart recorder as the Bragg angle is varied continuously by means of a small synchronous motor which drives the crystal and Geiger Counter arm.

Figure 4 shows the result when the sample consists of a mixture of two rare earth salts—samarium (62) and gadolinium (64). It is immediately apparent that even though the L series contains more lines than the K series there is no ambiguity about the identification of the constituents. The remaining elementary components of the salts above atomic number 22 could likewise be detected by measurement of their characteristic radiations from the sample. The relative heights of the lines depend on several factors and are not usually predictable with accuracy from the percentages of the constituents in the mixture alone.

Figure 5 shows how the measured intensity of K series radiation varies with atomic percentage of iron in alloys of iron with aluminum (13), with nickel (28) and with silver (47). For quantitative analysis, then, one must make up control

samples for calibration purposes, as is necessary with optical spectroscopy. The only particular care required in excitation of the sample is that the primary x-ray intensity must be maintained constant. This is most easily accomplished by electronic regulator systems for the x-ray tube voltage and emission current (Le Mieux and Beeman, 1946; Pepinsky and Jermotz, 1948).

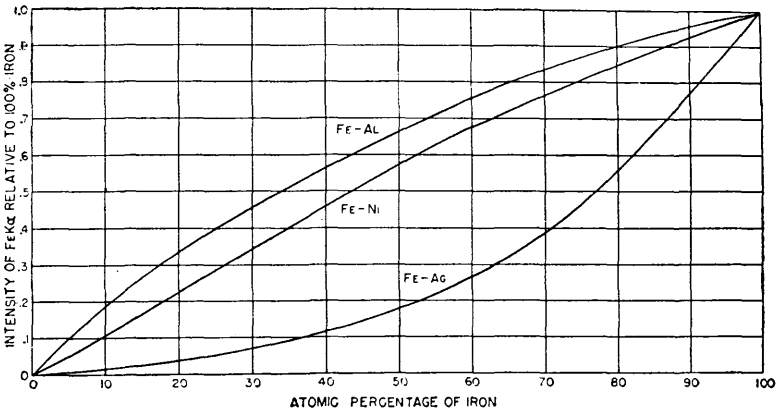


FIGURE 5. Relative intensity of FeK $\alpha$  radiation *versus* atomic percentage of iron in mixtures with aluminum, nickel and silver (after Friedman, 1948).

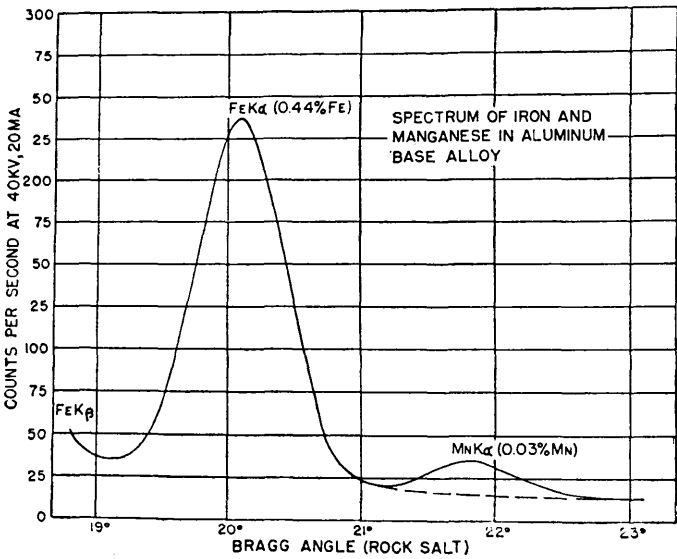


FIGURE 6. Spectrum of iron and manganese in an aluminum base alloy. (After Friedman, 1948).

Figure 6 illustrates the sensitivity of the method. The reader is referred to the original article for details of the investigation. It will be noticed that in this exploratory investigation the apparatus was an assemblage of components not specifically designed for this particular application.

The North American Philips Company has recently placed upon the market a complete fluorescence analysis unit specifically designed for analysis above atomic number 20.

It would be of great advantage to be able to extend the wavelength region. By going to 5.5A, for example, all atomic numbers greater than S(16), including those between Mo(42) and Cs(55), inaccessible to Friedman, would be made available without exceeding 45 KV on the x-ray tube. If the region could be extended to 12A, the practical limit for crystals, the atomic number range would include Na(11). This would necessitate placing sample and spectrometer in a chamber which may be evacuated. Notice that the x-ray tube itself need not be in the chamber.

The main difficulty encountered is that Geiger counter tube windows would have to be designed to withstand both the inward atmospheric pressure and the outward zero pressure of the evacuated chamber and at the same time be so thin that the long wavelength radiation will be satisfactorily transmitted. This seems to be an unreasonable requirement for the Geiger Counter, hence the interest in the scintillation counter, which has no window.

Recently West, Meyerhoff, and Hofstetter (1951) have described experiments on the measurement of x-ray intensities to 6A with single, optically clear crystals of NaI sensitized with thallium. These crystals, suitable for scintillation counters, are obtainable from The Harshaw Chemical Company. They are hygroscopic and extremely poisonous. The hands must be washed immediately after handling this material and care taken that none of the dust is inhaled. They may be stored and cleaved under Nujol. It is entirely possible that the crystals may be satisfactorily coated against atmospheric moisture by dipping them into a solution of polystyrene in benzene and allowing to dry. It is already known that their performance is not impaired by a coating of Nujol (Hofstetter and McIntyre, 1950).

There seems to be no obvious reason why the atomic number range should not be extended to make ultimate qualitative and quantitative analysis under favorable circumstances (Clark, 1940), a simple, straightforward procedure for the large majority of chemical elements.

#### ULTIMATE ANALYSIS BY ABSORPTION

In certain cases of quantitative analysis the preparation of a control sample to use with the emission method is either inconvenient or impossible. Many ores would furnish satisfactory examples of the former and that rarest of elements (Dushman, 1951) Pm(61) would clearly fulfill the latter. In this case one might add a small known percentage of the element in question (or one of its neighbors in the periodic table) to the finely powdered sample and observe the change of intensity of some convenient line. However, Coster and Nishina (1925) found this not always to be a reliable procedure.

To circumvent these difficulties Glocker and Frohnmayer (1925) proposed measuring the absorption edge discontinuities in the sample material and interpreting the result in terms of the percentage constitution.

Exploration of this method has resulted in some interesting applications. Indeed, the method has become so useful and successful that it has been given the name of *x-ray absorptiometry* (Liebhafsky, 1949, 1951). By this means Engstrom (1946) measured with an accuracy of 10 percent the calcium and phosphorus content of biological materials present in amounts between  $10^{-10}$  and  $10^{-11}$  gms. An automatic spectrometer for absorption spectrometric work has been constructed at the Dow Chemical Company (Frevel, 1948).

It is by no means necessary to use monochromatic x-rays in absorptiometry. Perhaps the greater number of applications of absorption in industry use the polychromatic radiation directly from the x-ray tube, or in some cases from the sample as secondary radiator. Industrial control processes have been in use for some time on the thickness of steel sheet in the rolling mill (Clapp and Pohl, 1948), the concentration of tetraethyl lead in gasoline (Michel and Rich, 1947; Sullivan

and Friedman, 1946), the thickness of tin plate on sheet steel (Beeghly, 1950), and many other applications which the reader will find upon examining the literature.

#### COMPOUND ANALYSIS

As indicated earlier in this report a crystalline substance is made up of a regular array of atoms or molecules. The number of possible fundamental arrangements is fairly small and has been the subject of extensive study by crystallographers

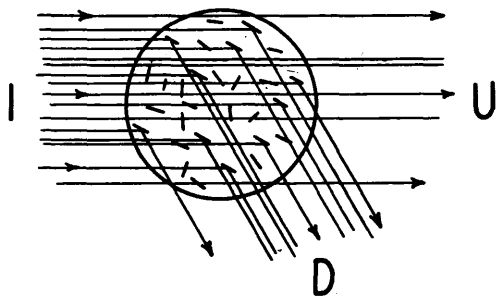


FIGURE 7. Diffraction of a monochromatic x-ray beam by randomly oriented microcrystals of a finely powdered sample. One of the possible diffraction directions is shown. Notice that all effective crystal planes are parallel. I, incident parallel beam; U, undiffracted beam; D, diffracted beam.

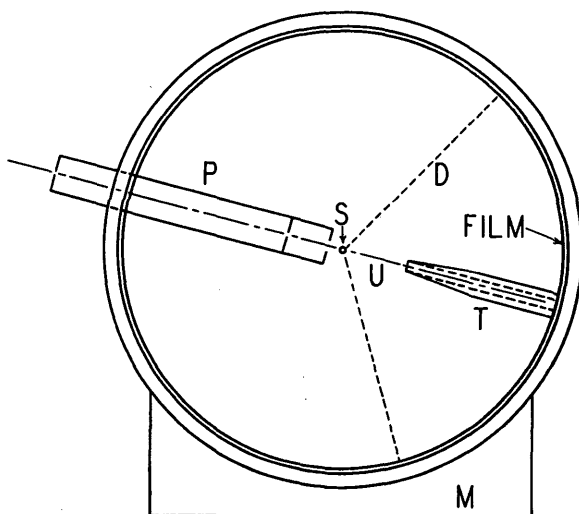


FIGURE 8. Schematic diagram of powder diffraction camera. P, pinhole system; S, powdered sample; U, undiffracted beam; D, diffracted beam; T, trap for the strong undiffracted beam; M, mounting pad. The photographic film is placed around the inside of the camera.

(Clark, 1940). In any one of the fundamental arrangements layers of atoms or molecules can be discerned in various directions in the crystal, the distance between layers depending on the particular direction chosen. An instructive comparison is furnished by the standard orchard arrangement (or corn, for the middle West reader!). If one stands in the middle of the orchard he can see rows of trees in selected directions, the distance between rows depending on the particular direction chosen.



It is a remarkable fact that a particular chemical compound, upon crystallizing, characteristically does so in one or sometimes two of the possible arrangements; and even though two different compounds may choose the same arrangement they always have different values of the atomic layer separations. Hence an identification in an unknown crystalline sample of the type of arrangement and a measurement of the so-called lattice parameters would provide complete identification of the chemical compound. However, as we shall see, it is not necessary to gather even this much information to identify the compound uniquely.

If, now, a monochromatic beam of x-rays is incident upon the crystal, reflection of the beam will occur whenever the angle of incidence on one of these atomic planes satisfies Eqn. 1. To get all the various possible reflections the crystal would have to be oriented in a number of different directions. The Debye-Scherrer method of x-ray crystal analysis uses the sample in finely powdered form, and for this reason is also known as the powder diffraction method (Clark, 1940). In any position of the crystalline mass there will always be some of the randomly oriented minute crystals in just the right position to reflect the incident monochromatic beam of x-rays from any given set of parallel atomic planes. Figure 7 shows a sample diffraction on a magnified scale and figure 8 gives the essential arrangement of a powder camera with photographic registration. The powder diffraction pattern of molybdenum is shown in figure 9.

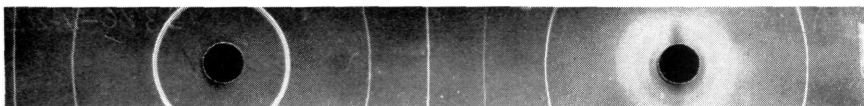


FIGURE 9. Powder diffraction pattern of molybdenum metal taken with Fe  $K\alpha$  radiation. The  $K\beta$  has been eliminated by suitable filtering of the x-ray beam. (Courtesy of Battelle Memorial Institute, Columbus, Ohio.)

The question may occur to the reader as to just why the powder method is adopted for most analytical work. The reasons are several. The powder method is a simple experimental technique with uniquely interpretable results. In perhaps the majority of cases the sample is presented to the analyst in powdered form. If not, the sample can usually be powdered by grinding or filing. However, in those cases where the sample must not be disturbed single crystal techniques may be used.

Prior to 1938 if one wished to use powder diffraction patterns for chemical analysis he had to identify the crystal type from the pattern, work out the lattice parameters and then chemically identify the crystal from tables of lattice constants worked out by crystal analysts. In that year, Hanawalt, Rinn and Frevel (1938, 1944) published the first table listing not only the grating spaces corresponding to the several lines in the pattern but also their relative intensities (Sproull, 1946). These authors showed that only a moderately accurate measurement of the  $d$  values of the three most intense lines in a given pattern is enough to allow unique chemical identification from their tables. Since that time the number of compounds listed by American Society for Testing Materials has grown to approximately 5000.

In the early 1940's Dr. Herbert Friedman of the Naval Research Laboratory investigated the application of the Geiger Counter to the direct measurement of powder diffraction patterns with excellent results. This work subsequently led to the development of the North American Philips Geiger Counter Spectrometer through the cooperative efforts of Dr. Friedman and the Company's laboratory. A picture of this unit is shown in figure 10. It uses the Bragg spectrometer principle with a powdered crystalline reflector, which, of course, is the sample under investi-

gation. We are prepared now to consider this case more fully. In figure 11, FS is the extended focal spot of the x-ray tube giving monochromatic radiation. Two defining rays are shown of the radiation from FS which gets through the fairly fine slit. Notice that all the radiation from the target which gets through the slit is confined within the angle  $\alpha$ . Beyond the slit the rays spread out and bathe the powdered sample plate PS. Those rays which arrive near A are sure to find small crystals oriented at the Bragg angle and will be reflected. The same is true at B and indeed in every region of PS receiving radiation in the angle  $\alpha$ . The



FIGURE 10. North American Philips Geiger Counter X-Ray Spectrometer. The vertical scanning Geiger counter is seen at the right. Mounted for simultaneous use are the Weissenberg Goniometer and two powder diffraction cameras.

reflected radiation from all parts of the plate proceeds to a "focus" at F symmetrical with the slit S. We place a slit at F and allow all x-rays passing through to enter the ionization chamber. In this case, then, the position of the powdered crystal plate is of only secondary importance and we measure carefully the angular position of the ionization chamber slit. This gives us  $2\theta$ , or twice the Bragg angle.

The Philips instrument has the advantages of excellent sensitivity, a permanent record traced out on an automatic chart recorder, very accurate intensity measurements, flexibility and speed.

Here, however, we must put in a word of caution. So long as we are interested strictly in chemical qualitative and quantitative analysis in the ordinary sense the

Geiger Counter Spectrometer is doubtless unsurpassed. However, the broader aspects of chemical analysis, in which we may be interested in problems such as particle size (especially if it is large), orientation, work hardening of metals, and so on, have special requirements which are oftentimes answered far better by the photographic film (Clark, 1940). We see that the Geiger Counter is a special tool which answers some needs admirably but offers no panacea.

There is under construction at the present time in the author's laboratory an x-ray spectrometer of modified design, which may have some application in x-ray compound chemical analysis (Broussard, 1950). The arrangement is shown schematically in figure 12. It is seen to be essentially a "double crystal" spectrometer. The characteristic x-rays from the copper target are reflected by the

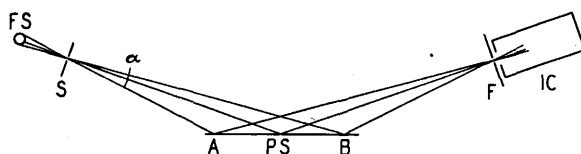


FIGURE 11. Schematic diagram of Bragg powdered crystal spectrometer. FS, focal spot of the x-ray tube; S, source slit; PS, powdered sample spread out on glass plate; F, focal line slit; IC, ionization chamber or Geiger Counter.

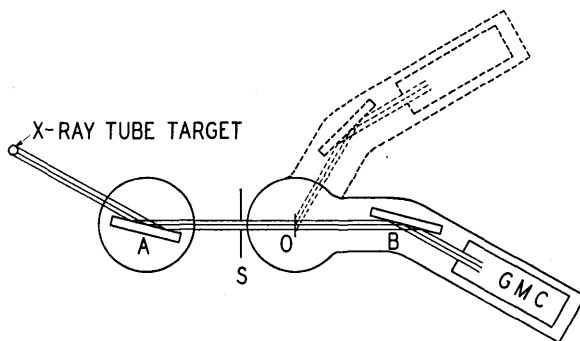


FIGURE 12. Double crystal powder diffraction spectrometer. X-ray tube target to give strong line radiation (e.g., copper); A, B, large single crystals (e.g., calcite or rock salt); S, defining slit to eliminate  $K\beta$ ; O, powdered sample; GMC, Geiger Counter.

first crystal A to the sample under investigation situated on the axis O. Actually, because of the difference in Bragg angle only the  $K\alpha_{1,2}$  radiation will reach the sample, the  $K\beta$  radiation being eliminated by the shield S. The second crystal B and the Geiger counter are mounted to move together about the axis O and to be so related that any Cu  $K\alpha$  radiation reflected by B will enter the Geiger Counter. The spectrometer is designed to function in the so-called "parallel" position (Compton and Allison, 1934). As the arm is made to travel around, then, by means of a synchronous motor drive, the detector will record in succession the diffracted beams, such as the dotted one in figure 12. The resolving power of this spectrometer is extraordinarily high—of the order of 10,000 as a maximum—and the line widths are correspondingly small. Any abnormally large line widths will indicate a small average crystalline size for the sample. Indeed, a line width measurement can be interpreted in terms of average particle size.

Because of the extremely narrow lines their position may be determined with great accuracy. This will allow studies on the minute changes produced in the grating spaced under certain conditions, such as the alloying of metals, intra-

granular elastic distortion produced by external stresses, and the like. This equipment should also be applicable to the study of liquid sample diffraction, and diffraction by organic substances. The particular geometry used will all but eliminate difficulties due to fluorescence of the sample.

In powder diffraction work one is always limited by the available intensity of x-rays from the source. Recently, a very ingenious cathode designed by Heil and Ebers (1950) has been adapted to the production of x-rays (Shaw and Soules, 1951). The advantage of this cathode is that it gives extraordinarily intense electron emission in a parallel beam of small cross-section. The beam is approximately 2 mm. in diameter and up to 500 ma. Work is being started to use the cathode in a rotating anode, water cooled x-ray tube designed to give a maximum of 500 ma into the focal spot (7 mm x 10 mm) at 30 KV target potential. This makes a continuously operating x-ray tube of approximately 15 KW target dissipation. The x-ray intensity increase over standard diffraction tubes in use now will be a factor between 10 and 20. The tube, of course, will be continuously pumped and many technical difficulties must be solved before it can function.

X-ray analysis has become a standard technique to be considered on a level with other analytical techniques. Its range of application is still limited, partly because of the fact that time is required to explore the possibilities and partly by instrumental limitations. Problems of the latter type are being attacked energetically by many researchers. The needs are quite clear and one may expect that instrumentation will continue to improve.

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